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14. ABSTRACT Present and anticipated variation in jet propulsion fuels due to advanced engine compression ratios and airframe cooling requirements necessitate greater understanding of chemical phenomena associated with the feed system and combustion aspects of the airbreathing propulsion systems under consideration by the U. S. Air Force. With AFOSR support an integrated, fundamental research program had been established at Princeton. The focus during the subject period was directed to understanding the pyrolysis and combustion of endothermic fuels under subcritical conditions and the pyrolysis of these fuels under supercritical conditions. Main consideration was given to methylcyclohexane, decalin and tetralin, which are not only endothermic fuels, but alkylcyclohydrocarbons, the naphthene components of JP fuels. The subcritical conditions in the study were 0.1 MPa (1 atm) and temperatures ranging between 900-1200 K. The supercritical conditions were between 4-9 MPa (40-90 atm) and 720-820 K. The Princeton Turbulent Flow Reactor was used for the subcritical studies and a newly designed coiled tubular reactor for the supercritical studies. Substantial experimentation and analytical evaluation revealed distinct differences between the subcritical and supercritical results. From the rate of fuel decay under the conditions described, it was determined that, although the activation energies were of the same order, the supercritical (4.5 MPa) pre-exponential factor A was two orders of magnitude greater than the subcritical (0.1 MPa) one. Further, not only were complete scission products of all these fuels found for both cases, but, interestingly, cyclo-intermediates were found under supercritical conditions as well. As the supercritical pressure was increased, the ratio of cyclo-intermediates to scission products increased. Additional experimentation revealed that these cyclo compounds lead to the polycyclic aromatic hydrocarbons which are the precursors to particulate formation. The formation of the product cyclo-hydrocarbons was attributed to the phenomenon known as caging.					
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FUELS COMBUSTION RESEARCH:
SUPERCRITICAL FUEL PYROLYSIS

Prepared by:



Irvin Glassman
Robt. H. Goddard Professor,
Principal Investigator

Princeton University
Department of Mechanical and Aerospace Engineering
Princeton, NJ 08544

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Abstract

Present and anticipated variations in jet propulsion fuels due to advanced engine compression ratios and airframe cooling requirements necessitate greater understanding of chemical phenomena associated with the feed system and combustion aspects of the airbreathing propulsion systems under consideration by the U.S. Air Force. With AFOSR support an integrated, fundamental research program had been established at Princeton. The focus during the subject period was directed to understanding the pyrolysis and combustion of endothermic fuels under subcritical conditions and the pyrolysis of these fuels under supercritical conditions. Main consideration was given to methylcyclohexane, decalin and tetralin, which are not only endothermic fuels, but alkylcyclohydrocarbons, the naphthene components of JP fuels.

The subcritical conditions in the study were 0.1 MPa (1 atm) and temperatures ranging between 900 and 1200 K. The supercritical conditions were between 4 and 9 MPa (40-90 atm) and 720 and 820 K. The Princeton Turbulent Flow Reactor was used for the subcritical studies and a newly designed coiled tubular reactor for the supercritical studies. Substantial experimentation and analytical evaluation revealed distinct differences between the subcritical and supercritical results. From the rate of fuel decay under the conditions described, it was determined that, although the activation energies were of the same order, the supercritical (4.5 MPa) pre-exponential factor A was two orders of magnitude greater than the subcritical (0.1 MPa) one. Further, not only were complete β scission products of all these fuels found for both cases, but, interestingly, cyclo-intermediates were found under supercritical conditions as well. As the supercritical pressure was increased, the ratio of cyclo-intermediates to β scission products increased. Additional experimentation revealed that these cyclo compounds lead to the polycyclic aromatic hydrocarbons (PAH) that are the precursors to particulate formation. The formation of the product cyclo-hydrocarbons was attributed to the phenomenon known as caging.

I. GENERAL SUMMARY STATEMENT

Princeton's efforts in its research program, "Fuels Combustion Research" were most recently concentrated on the pyrolysis and combustion of endothermic fuels and the pyrolysis of similar fuels under supercritical conditions. The motivation for this effort has been the Air Force's interest in advanced propulsion concepts and its plan for next generation aircraft gas turbines whose compressor ratios may be increased to the extent that the fuel lines feeding the combustors attain supercritical conditions. These corresponding interests led to an integrated research program that studied in detail the pyrolysis and combustion of methylcyclohexane and decalin at 1 atm pressure and the pyrolysis of these fuels, tetralin, and others under supercritical conditions. The experimental techniques employed were the Princeton Turbulent Flow Reactor, which had been described in detail in numerous previous AFOSR reports and archival papers, and a simple, unique, supercritical flow reactor developed during the recent efforts of the program.

II. INTRODUCTION TO THE OVERALL RESEARCH EFFORT

The envisioned cooling demands of next generation high-speed aircraft far exceed the capacity of current aircraft cooling technologies. The high heat loads imposed on the fuel, which is the main coolant of modern high-speed aircraft, may result in fuel degradation. If the heat-absorbing capacity of contemporary fuels is not enhanced, then, at the envisioned residence times, pressures, and temperatures of these next generation fuel systems, fuels will decompose into harmful intermediates and solids. Solid formation can result in fuel line blockage or serious engine damage. One solution to this problem is to utilize a fuel that has the potential for both sensible and chemical heat-absorption; current fuel systems utilize sensible energy absorption exclusively. This approach is the one behind the concept of an endothermic fuel, a fuel that undergoes a controlled heat-absorbing chemical reaction prior to combustion. Three such endothermic fuels, methylcyclohexane, decahydronaphthalene (decalin) and tetrahydronaphthalene (tetralin) had been the main subjects of the reported investigation.

In what appears to be the Air Force's version of next generation aircraft, not only endothermic fuels but perhaps all types of fuels will be subject to extreme conditions of temperature, pressure, and residence time (1). These conditions will simultaneously exceed the critical temperature and pressure of most hydrocarbon fuels that are liquids near standard conditions and render the fuel a supercritical fluid (as noted by the current leading effort at the Air Force Research Laboratory Propulsion Directorate (1)). The high temperatures and pressures could, in some regions, create liquid-like concentrations of a supercritical fluid. These conditions could result in a reaction environment that incorporates features of gas phase and liquid phase chemistry as well as some characteristics unique to supercritical fluids. Supercritical fluid transport coefficients, in many cases, are gas-like; however, supercritical solvation effects and caging effects had been commonly associated with liquid-phase chemistry. Unfortunately, pyrolytic reactions in a supercritical environment had not been as well characterized as reactions in a gas or a liquid medium. The subject program had concentrated, mainly, on the supercritical pyrolysis mechanisms of methylcyclohexane, decalin and tetralin over a range of conditions

representative of the most extremely possible envisioned for next generation aircraft fuel systems. A large part of the latest aspect of the program considered decalin and tetralin, which have two possible implementations for improving fuel thermal stability: 1) as endothermic fuels and 2) as hydrogen donor additives.

The use of decalin or tetralin to improve fuel thermal stability was as a hydrogen donor additive to stabilize chain-carrying radicals and to promote the formation of saturated products. H-donor additives had been shown to effectively diminish or eliminate solid formation in the pyrolysis of actual jet fuels at representative aircraft fuel system conditions (2) and had long been a mainstay of the coal liquefaction process (3). Previous components of this general effort had shown that it had implications for understanding the formation of high order PAH. In an envisioned supercritical environment, hydrogen donor additives could take advantage of the comparatively slow β -scission times of hydrocarbon pyrolysis below 800 K and the high concentrations of the supercritical state. Both of these factors may contribute to the effectiveness of the hydrogen donor. High concentrations increase the probability of an H-transfer reaction stabilizing a radical at a saturated product through bimolecular collision, and slow β -scission times decrease the probability of unimolecular decomposition. Furthermore, compared to liquid phase reactions, the enhanced molecular transport of the supercritical fluid could increase the probability of an unstable radical encountering a suitable H-donor. To assess the potential effectiveness of these additives, the stability of pure n-decane was compared to n-decane in a bath of the hydrogen donor molecules decalin and tetralin under representative supercritical conditions.

As stated, reactions in a supercritical medium had not been nearly as well characterized as were reactions in a conventional gas-phase combustion system or a liquid-phase reaction in solution. Supercritical fluids can have drastically different transport and solvation properties compared to a gaseous or liquid medium. These effects could, for example, influence a diffusion-controlled reaction or sustain large solid precursor molecules in solution (1). In addition, solute/solvent interactions, which are virtually insignificant in gas-phase pyrolysis, could result

in different decomposition pathways than had been observed in the gas phase. For example, Melius, et al. (4) found that a supercritical solute/solvent interaction could influence the rates of the water gas shift reaction in supercritical water. At very high concentrations, solvent water molecules assisted in the formation of the transition-state. They found rates that were strongly concentration- and temperature- dependent. In addition, near the critical point, although not an area of current or proposed experimentation, it is to be noted that "clustering" phenomena can result in reaction rates that are orders of magnitude higher than those found in the gas phase (5). Poutsma (6), for example, had noted that supercritical tetralin pyrolysis is mechanistically similar to liquid-phase tetralin pyrolysis, but differs from that observed in the gas phase.

In the overall Combustion of Fuels program, some early experimentation under supercritical conditions for methylcyclohexane pyrolysis had been carried out and reported (7). In these early studies, refinement of the analytical techniques had not been fully developed, nor had the ability to determine whether or not particulate formation occurred. When these conditions were resolved, the approach was to determine whether or not particulate formation could be traced. In reality, a check to evaluate the capability of the improved supercritical reactor system changes was performed (8,9). Consequently, measurements with respect to PAH formation, the precursors to particulates, and actual particulate formation were more recently made under conditions ranging from 540 to 592 K and pressures from 27 to 36 atm (2.7 to 3.6 MPa). The actual results are reported in Fig. 1. As one will note from this figure, PAH and solid formation was observed for the endothermic fuel, methylcyclohexane and 10/90 molar % of heptane and toluene. Yet, essentially no PAH or solid formation was found for neat heptane or toluene. The results were readily explained in that toluene does not pyrolyze below 840 K due to its high resonant stabilized bond strengths and pure heptane breaks down almost completely into benign gaseous products. However, for the mixture the radicals formed during the heptane pyrolysis provide the necessary abstraction reaction to facilitate toluene growth to PAH. These results verified the fact that the apparatus and analytical techniques had been improved to the

point that extensive PAH and other complex hydrocarbon species could be measured quantitatively and particulate formation could be identified.

The AFOSR program was then redefined to analyze whether or not differences could possibly occur between atmospheric and supercritical measurements. In particular, the focus was on four elements: what, if any, intermediates and products would form under supercritical conditions that did not form under sub-critical conditions; what would be the effect of varying pressure under supercritical conditions; how would the rates of fuel pyrolysis compare and how do the physical parameters affect particulate formation. In an integrated research effort approach, the main consideration was initially given to methylcyclohexane, decalin and tetralin. No evaporator was available for tetralin in the one atmosphere reactor, but, nevertheless, the supercritical results obtained contributed to understanding the direction that future work should take. To ensure clarity of this final report, it is appropriate to show in Fig. 2 that methylcyclohexane is the alkyl analogue of the aromatic toluene, decalin is the alkyl analogue of the aromatic naphthalene and tetralin has an alkyl-aromatic structure between decalin and naphthalene (a polynuclear aromatic hydrocarbon (PAH)).

Typical analyses of particular experiments that were taken are reported in Figs. 3 and 4, which are typical histograms of the major products of methylcyclohexane and decalin pyrolysis. Many such histograms had been obtained under various supercritical conditions and are the basis of the results discussed in the Section on Research Progress. These figures are reproduced in color to reduce the complexity for the reader. Not only can one visualize the various compounds formed, including PAH, but the red bars designate the compounds which were found to be a key to understanding the differences that occur between sub- and supercritical operation. The red bars in the methylcyclohexane histogram designate the species dimethylcyclopentanes, and the red bar in the decalin histogram designates methylhexahydroindane. The quality of such histograms produced confidence in the reactor, chemical analysis techniques, and the results to be reported.

III EXPERIMENTAL APPARATUS

A. Reactor System

The following description of the experimental apparatus and procedures solely details the supercritical experimental approach. Spectrophotometric grade fuels (99%+purity) obtained from Aldrich were used in all experiments. Purity was confirmed by gas chromatography. In order for pyrolytic reactions to be studied independently of any auto-oxidative effects, the fuels were de-oxygenated by a nitrogen sparge for a minimum of 3 hours with a nitrogen flow of 2 liters per minute through a maximum of 200 ml of fuel. This sparge time and flow rate displaced the dissolved oxygen content in the fuel to less than 1 part per million (10). Sparging allowed the pyrolytic chemistry to be studied independently of any auto-oxidative effects.

All experiments reported in the following sections were conducted in the isothermal, isobaric, flow reactor designed to approach the plug-flow idealization (Fig. 5). The reactor had been constructed particularly for the study of the kinetics of supercritical hydrocarbon pyrolysis (7-9). A high-pressure HPLC pump forced reactants through a capillary tubing coil immersed in a heated-fluidized alumina bath (Techne Model SBL-2D). The capillary tubing (1.59 mm OD, 0.051mm ID) was constructed of a silica-lined stainless steel (Silicosteel by Restek). Precisely controlled pressures as high as 11 MPa and temperatures as high as 860 K were attained. A water-cooled heat exchanger at the entrance and exit of the coil ensured a controlled thermal history and residence time. Quenched intermediates passed through a stainless steel 5-micron frit to filter out any solids and into a six-position multi-position valve. The collected samples were released from the multi-position valve into a gas/liquid separator. The gas was released into an evacuated teflon-lined gas sample bag; the liquid was released into a weighed sample vial.

The tubing dimensions and volumetric flow rates of reactant were chosen in order to closely approach the idealization of a plug-flow reactor using criteria validated by Cutler et al. (11). Binary diffusion coefficients for this analysis were calculated from Chapman-Enskog theory. Determination of the density of the supercritical mixture was determined using the NIST

code SUPERTRAPP (12). Pressure in the reactor was controlled by means of a dome-loaded back-pressure regulator located downstream of the multi-position valve. Uncertainty in pressure control was ± 0.2 MPa. Temperature was controlled by means of an electronic PID controller with a thermocouple sensing the center of the alumina bath. Uncertainty in temperature was ± 5 K due to the large size of the alumina bath and imperfect fluidization.

Verification of homogeneous chemistry was initially performed by means of a comparison of product yields from two different reactor materials (9). Nearly identical product yields and distributions were found in a comparison of pyrolysis results from experiments conducted with silica-lined stainless steel and a chromatography-grade 316 stainless steel at temperatures as high as 820 K. The observation of nearly identical results from drastically different wall materials suggested that the chemistry that occurred was independent of the wall material. All results shown later represent data from experiments conducted in silica-lined tubing.

B. Product Analysis by Gas Chromatography

Separate liquid and gaseous analyses were performed on a Hewlett-Packard 5890 Series gas chromatograph. The liquid samples were injected by means of a calibrated syringe onto a DB-5 column (J&W Scientific, 30 m, 0.32 mm i.d., 0.025 μ m film). The gas samples were injected into a 1 cc sample loop and then into a similar HP 5890 chromatograph. For the gaseous samples, C_4 and smaller species were separated by means of a PORA Plot-Q column (Chrompack, 25 m, 0.32 mm i.d., 10 μ m film) in conjunction with the DB-5. A flame ionization detector (FID) was used to quantify mole fraction of product yields. FID signals were converted to mole fraction by means of an extensive calibration. Calibrations were performed on as many as 22 liquid and 16 gaseous species, and results were generalized to the remaining 76 compounds based on number of carbon atoms. Many of the minor intermediates were not identified. Of the 114 compounds quantified, in most experiments, 75 have been identified. Analysis of the major intermediates and their yields gave some insight into the dominant kinetic pathways.

The analytical equipment used in this study did not have the ability to measure gaseous hydrogen, H_2 . However, it was not thought that hydrogen would be a major product. The difference in activation energies between C-H and C-C bonds is about 12 kcal/mole. Thus, unimolecular C-C bond breaking, β -scission, would be about 103 times faster than C-H bond breaking at the highest temperatures examined in this study. Because many reactive surfaces are known to catalyze H abstraction, significant hydrogen yields may be an indicator of catalytic effects occurring.

IV. RESEARCH PROGRESS

A. Experimental Results

As noted, various hydrocarbon fuels, which can be classified as undergoing endothermic pyrolysis, are being considered for next generation aircraft of interest to the Air Force. Methylcyclohexane, the prototype endothermic fuel, was the earliest focus of the long range program (9, 17). More recent efforts concentrated on experiments and models for the possible candidate endothermic fuels - decalin, tetralin and n-decane. In particular, their pyrolysis characteristics under sub- and super-critical conditions were studied to determine whether their chemistry would lead to particulate formation (fouling) in fuel lines. Since they must eventually undergo combustion in the engine, the importance of knowing their gas-phase reaction kinetics became an important element of the program and was investigated as well (18).

The supercritical decalin, tetralin, and decane pyrolysis mechanisms were determined as a function of temperature and pressure in the high pressure plug flow reactor. In addition, mixtures of 90% (molar) decalin with 10% decane and 90% tetralin with 10% decane were examined over a range of temperatures at a constant pressure of 3.13 MPa. Temperatures examined in each set of experiments ranged from around 700 K to 810 K. Typical pressures ranged from 0.2 to 10.0 MPa. Since the density of the reacting stream varied with temperature, pressure, and conversion, the residence time in the reactor varied.

Supercritical decalin pyrolysis was evaluated over a temperature range of 730 to 810 K at a pressure of 4.14 MPa (19). The major products of supercritical decalin pyrolysis at 810 K and a residence time of 62 seconds, listed in order of decreasing molar yield included: methane, propane, ethane, propene, ethene, butene, butane, methylhexahydroindane, and indene. The yield of products increased exponentially as temperature increased, characteristic of Arrhenius kinetics. A global activation energy, assuming pseudo first order reaction, of 276 ± 10 kcal/mole was determined for decalin decay from 730 to 810 K. The pre-exponential A factor found to be $10^{15.8 \pm 1.5} \text{ sec}^{-1}$. This analysis did not differentiate between the cis and the trans decalin isomers but considered their sum. The pseudo first order assumption was verified in additional experiments which examined decalin decomposition over a range of pressures at a constant temperature of 761 K. A global reaction order of 0.98 was determined, supporting the global pseudo first-order assumption. The results of these experiments will be discussed subsequently.

Supercritical tetralin pyrolysis over a range of temperatures from 702 K to 802 K at 4.77 MPa was also examined. At 802 K and a residence time of 79 sec., major products listed in order of decreasing yield included: naphthalene, methylindane, ethane, methane, ethene, phenylbutane, propane, propene, phenylpropane, ethylbenzene, and toluene. A pseudo first order global activation energy for tetralin pyrolysis was determined to be 273 kJ/mole, with a pre-exponential of $10^{15.9 \pm 1.5} \text{ sec}^{-1}$. A global reaction order of 1.01 was determined from experiments where pressure was varied at a constant temperature.

In order to assess the potential application of tetralin and decalin as H-donors, supercritical pyrolysis of mixtures of 10% decane in 90% decalin and 90% tetralin (molar percent) was also examined. These experiments were conducted over a temperature range of 700 to 800 K at a pressure of 3.13 MPa. Pure decane decomposition had the highest decay rate observed in this temperature range. Although it had the highest activation energy, its pre-exponential factor was much greater than that found in either of the mixtures.

Subcritical (1 atm) gaseous decalin pyrolysis results had been reported in Refs. 17, 20. The major pyrolysis products found under these conditions included large amounts of methane,

alkenes (ethene, propene, butadiene), and the aromatics benzene and toluene. Major products of supercritical decalin pyrolysis at 730-810 K and 4.14 MPa included similar light alkenes (ethene, propene, butadiene), as well as some benzene and toluene, especially at higher temperatures. However, the lower temperature supercritical pyrolysis also included an abundance of light alkanes, methylhexahydroindane, indene, indane, methylenecyclohexene, and cyclohexadiene, species not found in the one atmosphere higher temperature gas phase studies (19).

In the same temperature range as this investigation (770 K) and at one atmosphere, Ondruschka et al. (21) investigated gas phase decalin pyrolysis using laser heated pyrolysis and a quartz flow reactor. At 770 K, they found an abundance of methane, ethane, ethene, propane, propene, butene, butadiene, cyclical C₅ products, benzene, and methylenecyclohexene. Again, the major light olefins and alkanes observed in their work were consistent with the results found in this program. Although considerable similarity was found between the results of the Princeton study and that conducted by Ondruschka et al., at 770 K, a striking contrast between the one atmosphere and the supercritical study was found in the prevalence of methylhexahydroindane at supercritical conditions, a major product not found by Ondruschka et al., nor in this program's low pressure study at high temperature and in the relatively low yields of methylenecyclohexene in the supercritical pyrolysis. The differences in product distribution between the two studies conducted at the same temperature, but different pressures, indicated that the major reaction mechanisms of decalin pyrolysis could exhibit some pressure or concentration dependence.

Prior to a discussion of possible explanations for the pressure dependence of these reaction mechanisms, it is useful to consider in detail what the possible reaction pathways for some of the major products could be. As shown in pathways I to III of Fig. 6A and B, methylhexahydroindane formation is initiated by H-abstraction from any of the decalin C-H bonds. A subsequent β -scission creates a cyclohexane structure with two side chains, one olefinic, and one radical. The two side chains link by radical site addition to the double bond and, with H transfer from a neighboring molecule, methylhexahydroindane is formed.

Representative β -scission pathways for alkene formation are illustrated in pathways IV and V. Methylenecyclohexene formation as proposed by Ondruschka, et al. (21) is illustrated in pathway VI. Pathway VI is initially identical to pathway II. However, immediately after the β -scission, instead of the two side chains joining as in pathway II, a 1,5 H transfer which takes advantage of the mobility of the radical side chain shifts the radical site to the other ring. Subsequent β -scission results in methylenecyclohexene.

These mechanistic pathways were found to be revealing on how the pressure dependence of some of the dominant decomposition pathways could be occurring. Mechanistic pressure dependence was investigated in greater detail in a second set of experiments which examined decalin pyrolysis at a constant temperature of 761 K and a range of pressures (0.3 to 8.6 MPa). The mole fraction yields of methylhexahydroindane over yields of methylenecyclohexene as a function of pressure was found to be variable at a constant temperature of 761K. Clearly, methylenecyclohexene formation is favored at low pressure while methylhexahydroindane formation is favored at high pressures. Because these products appeared to be formed from the same or similar intermediates (pathways I-III and VI), a favorable concentration dependence for the ring contraction of pathways I-III over the 1,5 H isomerization of pathway VI and other alternatives to ring contraction could explain this trend. One explanation could be caging effects, as has been proposed in the program's earliest study (7) and had been commonly considered in the chemical process industry (22).

Similar to these decalin results were the earlier supercritical results of methylcyclohexane pyrolysis when it was postulated that the production of methylcyclopentane structures resulted from ring contraction (C_6 to C_5) from a cyclohexenyl radical, similar to the methylhexahydroindane formation mechanism mentioned. It was suggested for such cases that ring contraction could be influenced by a physical cage of molecules surrounding the C_6 radical, a consequence of the very high concentration environment associated with supercritical fluids or liquids. The cage promotes the formation of a more compact structure, a C_5 ring, and discourages the radical from opening up to form a larger, linear structure -- such as the large

radical intermediate of pathway VI of Fig. 6A for decalin, and its subsequent β scission decay. Correspondingly the competitive effects for methylcyclohexane are represented in a more simple fashion in Fig. 7. Thus, the postulate was that caging effects promote the ring contraction of pathways I-III (Fig. 6B) and discourage the formation of the large intermediate of pathway VI (Fig. 6A) and could be responsible for increasing yields of methylhexahydroindane and decreasing yields of methylenecyclohexene with increasing pressure.

In addition to having a use for development of possible reaction mechanisms, the data from this set of experiments was also used to measure global kinetic parameters. The measured global activation energy of 276 kJ/mole and global pre-exponential of $10^{15.8} \text{ sec}^{-1}$ show good agreement with those found in supercritical decalin pyrolysis studies at similar temperatures and pressures. For the program's one atmosphere gas-phase studies (17), a global activation energy of 217 kJ/mole and $A=10^{11.4} \text{ sec}^{-1}$ were determined.

Tetralin pyrolysis had been examined by many investigators for a variety of applications. Poutsma (6) reviewed many of these mechanistic studies of gas, liquid, and supercritical tetralin pyrolysis in the 650 to 1000 K range. Based on his review, expected major products of supercritical tetralin pyrolysis were methylindane, naphthalene, and butylbenzene. The major products of tetralin pyrolysis found in the current investigation over a temperature range of 702 to 802 K at a pressure of 4.77 MPa were in excellent agreement with those considered in other studies (6).

Just as supercritical decalin pyrolysis differed mechanistically from gas-phase decalin pyrolysis, Poutsma (6) argued that in a similar temperature range, supercritical and liquid tetralin pyrolyses appeared to follow different mechanistic pathways than gas-phase tetralin pyrolysis. For supercritical tetralin near 720 K and 4 to 10 MPa, similar to the conditions of this investigation, Poutsma argued that ring contraction (methylindane formation) dominated over dehydrogenation (naphthalene formation) and hydrogenolysis (butylbenzene formation); in contrast, Poutsma stated that gaseous tetralin pyrolysis in the same temperature range appeared

to be dominated by dehydrogenation, then ring contraction, and finally C₂ loss to form benzocyclobutene.

To further detail the effects of pressure on C₆-C₅ ring contraction in tetralin pyrolysis, as well as other effects, tetralin pyrolysis was examined at a constant temperature of 761 K and a range of pressures from 1.8 to 9.9 MPa. The variation of methylindane yield with pressure was very similar to that of methylhexahydroindane in the decalin pyrolysis. Like methylhexahydroindane, methylindane formation was heavily favored at higher pressures. The favorable tetralin ring contraction in a supercritical or liquid environment noted by other authors and found experimentally in this investigation was consistent with a reaction mechanism incorporating the caging effects currently under study.

The experimental evidence gathered for supercritical tetralin pyrolysis suggested a global activation energy of 273 kJ/mole and global pre-exponential of $10^{15.1} \text{ sec}^{-1}$ and compares well with the measured global decomposition parameters found for decalin, 276 kJ/mole and $10^{15.8} \text{ sec}^{-1}$. This result suggests that structural similarities between decalin and tetralin in the chemically active portions of the molecules may translate into some similarity in terms of reactivity.

Decane pyrolysis has been mechanistically well understood. It was examined to explore the potential application of decalin and tetralin as hydrogen donors to inhibit some pathways of pyrolytic decomposition and to afford fuels greater thermal stability. These types of molecules can easily donate hydrogen to an unstable radical to terminate a chain or to discourage the formation of unsaturated hydrocarbons, which can lead to solid formation.

For supercritical pyrolysis of neat decane, major products were completely in accord with traditional pathways associated with conventional gas phase alkane pyrolysis. Radical β -scission formed 1-alkenes and smaller radicals. Smaller radicals could stabilize through an H-transfer reaction or an addition reaction to form an alkane. They also could isomerize (for example, the 1,5 H-shift isomerization), or undergo additional scission reactions to ultimately form an abundance of ethene and methane.

However, in striking contrast to conventional gas phase subcritical hydrocarbon pyrolysis which was dominated by the formation of light olefins, under supercritical conditions a much greater yield of alkanes was found, along with reduced yields of ethene and 1-olefins. This observation was consistent with the fact that the ratio of the rates of H-abstraction to β -scission, normally much less than one, increases by a factor of around 50 over atmospheric pyrolysis at the same temperature due to the high concentrations of the supercritical fluid (at 4.5 MPa). For example, using representative rates of scission and abstraction from Allara and Shaw (23), at 750 K and one atmosphere, $k_{\text{abstraction}}[\text{RH}]/k_{\text{scission}}=0.04$. However, at 750 K and 4.5 MPa, supercritical conditions, $k_{\text{abstraction}}[\text{RH}]/k_{\text{scission}}=1.7$. Thus, the comparatively high yields of alkanes in the supercritical state were entirely due to higher [RH], which would come about from caging.

Global kinetic parameters describing pure decane pyrolysis were found to be $E_A = 269$ kJ/mole with an A factor of $10^{15.1} \text{ sec}^{-1}$ (21). This global activation energy is slightly below the activation energies of decalin or tetralin, 276 kJ/mole and 273 kJ/mole. This difference, in conjunction with a pre-exponential which was nearly equal in all cases (equal within the experimental uncertainty), suggested that decane was not quite as thermally stable as was decalin or tetralin under these conditions.

Finally, it appeared that the addition of tetralin or decalin to decane resulted in a slight improvement in the thermal stability of decane, consistent with the results found by Song et al. (2), who examined the stability of n-tetradecane with tetralin as an H-donor additive. Experiments conducted with mixtures of 10% decane in 90% decalin or 90% tetralin revealed that decane in the mixtures had conversions greater than a few percent at slightly higher temperatures than did neat decane. For example, a 30 percent conversion was reached at temperature of 770 K for the neat fuel, but was not reached until temperatures above 790 K in the decane/H-donor blend. Rates of global decane decomposition were higher for neat decane than for decane in decalin or tetralin. Rates of decane decomposition in the two mixtures were nearly equal within the given experimental uncertainty.

B. Review and Analysis of Experimental Results

Figure 8 reports the global kinetic rate data discussed in the preceding section (under 0.1 MPa and 4.5 MPa conditions) for the first order decomposition of three of the endothermic fuels. Fig. 9 summarizes the kinetic results and lists the rate constants and major products which were also discussed in the preceding section. The reported results were obtained from detailed chemical analyses and for the supercritical case derived from numerous histograms, such as those in Figs. 3 and 4. The significance of the histograms in Fig. 3 and 4 is now emphasized. Dimethylcyclopentane was not formed in the 0.1 MPa studies with respect to methylcyclohexane, and methylhexahydroindane is not formed in the 0.1 MPa studies of decalin. From an examination of the activation energies of all systems reported in Fig. 9, one would note that all except the subcritical study of decalin are in the 270 kJ/mole range. The statistical analysis of the experimental subcritical results required reporting the results stated; however, since all the other results reported values around 270 kJ/mol. From examination of Fig. 2 one would expect similar initial bond breaking under the subcritical decalin condition compared to the other cases. Thus one would expect that the true experimental activation energy value would also be in the 270 kJ/mole range. To keep the actual energy values within the proper range the pre-exponential A factor would have to be of the order 10^{13}sec^{-1} , as existed for the subcritical results for methylcyclohexane. The subcritical results then gave an A factor of 10^{13}sec^{-1} , while the supercritical results gave an A factor of 10^{15}sec^{-1} , and all the activation energies were essentially similar. This two-order-of-magnitude difference in the A factor may be significant and will be considered subsequently.

As depicted in Fig. 9, the subcritical (gas phase) methylcyclohexane pyrolysis results revealed that methylcyclopentane pyrolysis was β scission-dominated. Little, if any, PAH was found during the pyrolysis, and the major products were ethene, 1,3 butadiene, methane, and propane. Shown in Fig. 7, as well, is the general pyrolysis mechanism proposed and essentially validated. A detailed mechanism had been presented in the recent Ph.D. thesis of Zeppieri (17). Throughout this report, an effort has been made to refrain from presenting detailed mechanisms containing hundreds of reactions and their corresponding rate data. Instead, the key mechanistic

steps which represent the best insight to the fundamental concepts presented and, of concern, to the new research proposed only have been presented. Characteristic of such an effort is the general pyrolysis mechanism of methylcyclohexane reported in Fig. 7. Fundamental to subsequent discussion is the fate of the methylhexadienyl radical, designated MHL in Fig. 7.

From the representation in Fig. 3 and 9, with regard to methylcyclohexane, it was concluded that, while β scission processes were still important under supercritical conditions, they were significantly slower. Further, dimethylpentanes and methylcyclopentane were major products not found under subcritical conditions (Figs. 3, 7 and 9). Consistent with the similarity of the activation energy results presented in Fig. 9, the general steps to the formation of MHL remained the same as depicted in Fig. 7. Note, however, in Fig. 7, it was proposed that dimethylpentane developed from its corresponding MHL radical. The process by which the initial 6-member ring was converted to a 5-member ring was most apparently due to the phenomenon of caging, a phenomenon frequently discussed in the supercritical chemical process literature (22).

Under supercritical conditions, methylcyclohexane pyrolysis creates MHL which then follows two possible routes to further change: β scission, leading essentially to innocuous products or a cyclization due to caging and possibly leading to significant PAH formation. Obviously, the extent of either route depended on the physical parameters of the experiments.

To understand caging, it is best to consider both routes simultaneously. To offer a simple phenomenological approach, consider that in the dissociative β scission process, the products of any β scission step must diffuse away in competition with a collision process that would cause a radical such as MHL to form a new bond instead of breaking one and create a cyclohydrocarbon compound. This process would most likely occur under very high pressures. In a practical system the amount of PAH and subsequent particulates that form would be due to the competitive "rate processes," one controlled by the diffusion of dissociated species (β scission) and the other by a collision rate process that forms a new bond (caging).

A similar competition occurred in the case of decalin, and the comparison of the results was similar to the methylcyclohexane results. As shown in Fig. 6, decalin during supercritical pyrolysis, formed methylhexahydroindanes via methylhexadienyl radicals, and these precursors were available to form PAH and particulates. Also shown in Fig. 6 are two subcritical mechanisms, one proposed in this study (24) and the other by another investigator (21).

In order to estimate the effect of caging with respect to a chemical process, the general approach had been to apply transition state theory (22, 25). What essentially had been considered in general transition state theory (25) was the rate of formation of a product through an intermediate (complex) in competition with the intermediate reforming the initial reactant. β scission was considered as the competitive mechanism. The current effort hypothesized that the intermediate did not proceed back to the reactant, but had two possible routes to form different products. One route was β scission to innocuous products, and the other was a caging process leading to products which could cause fuel line fouling.

Following the classical chemical approach to evaluating a given route, under supercritical conditions PAH formation would be determined by the ratio of the collisional rate of formation of the new cyclohydrocarbon due to caging to the diffusion rate of the β scission products "to get out of the cage". This ratio was represented by the following expression:

$$\frac{v d^2 \exp(-E/RT)}{D} \quad \text{or} \quad \frac{v \exp(-E/RT)}{(D/d^2)}$$

where v is the collision frequency (sec^{-1}), d^2 the collision cross section, E the activation energy and D the mass diffusivity (cm^2/sec)(22). Essentially vd^2 is the pre-exponential kinetic A factor of the rate expression in the numerator. The second representation above was formulated so that a ratio of characteristic times was presented. This time ratio was recognized as a Damkohler number (22). For the pyrolysis processes under consideration in this effort, the caging instituted a bond formation process, and thus the activation energy was zero. Thus the relevant Damkohler number is $[v/(D/d^2)]$.

Typical small molecular diffusivities had been reported to be from 10^{-1} cm²/sec for gases to 10^{-5} cm²/sec in liquids (22). Under the supercritical conditions of the experiments discussed here, the diffusivities of a supercritical fluid would be somewhere between the two values, say of the order 10^{-3} cm²/sec. It was very tempting to speculate that the two-order-of-magnitude differences in A factor found between the sub- and super-critical conditions reported in this research is due to two orders of magnitude difference between the diffusion under sub and supercritical conditions, but there was no real justification for this comparison. Although supercritical fluids have, in many instances, greater similarity to liquids than gases, their diffusivities act more like gases in that they are inversely proportional to pressure. The diffusivities of liquids are independent of pressure. Certainly, these statements are true for the range of supercritical pressures in this study. Thus, caging products should increase with pressure. The ratio of intermediate methylhexahydroindane formation to the β scission route of decalin through methylcyclohexane was measured, as mentioned in the preceding section, as a function of pressure for a given temperature. The results are presented in Fig. 10. There was a substantial increase in methylhexahydroindane with a pressure increase, nearly an order of magnitude increase with a pressure increase from 0.1 to 8.5 MPa. These results are of great significance, not only because a small amount of particulates could play havoc in an aircraft gas turbine fuel line, but also because they offer fundamental confirmation of the processes proposed and illustrate the important parameters which a design engineer must consider.

It has been inferred that the real precursors to particulates would and/or had formed. The necessary data to develop the concepts presented so far were best obtained with relatively low reactor residence times. To validate the projections put forth, experiments with methylcyclohexane at 820 K and 82 atm were performed with reactor residence times that approached 120 secs. The results are reported in Fig. 11 and clearly show that the known precursors to particulates, such as soot, readily form.

V. SUMMARY AND CONCLUSIONS

Experimental studies of the pyrolysis of endothermic fuels, particularly alkylcyclohydrocarbons, under sub- and super-critical conditions revealed distinct differences between the two fluid states. Although the reaction rate constants under the diverse conditions examined were found to have the same activation energies, the pre-exponential rate A factor was found to be about two orders of magnitude greater for the super-critical condition. The product distribution for the super-critical condition revealed intermediates that led to the formation of polycyclic aromatic hydrocarbons that lead to the formation of particulates. It was further concluded that the existence of particulates was directly related to the time exposure of the fuel to the particular supercritical condition. This result is of greater importance to the design engineer developing aircraft gas turbines engines whose compression ratios would create super-critical conditions in the fuel line to the engine combustion chamber.

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PERSONNEL

Professor I. Glassman, Principal Investigator

Dr. Kenneth Brezinsky, Co-Principal Investigator

Mr. John F. Stewart, Graduate Student

Mr. Stephen P. Zeppieri, Graduate Student

Mr. Joseph Sivo, Senior Technician

PUBLICATIONS

Zeppieri, S. P., Brezinsky, K., and Glassman, I., "Pyrolysis Studies of Methylcyclohexane and Oxidation Studies of Methylcyclohexane/Toluene Blends." *Combustion and Flame* 108, 266 (1997).

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Glassman, I., Stewart, J. F., and Zeppieri, S. P., "Sub- and Super-critical Pyrolysis of Endothermic Fuels," Eastern States/Combustion Institute Meeting, Paper No. 145. October 1999.

PRESENTATIONS

Brezinsky, K., "Supercritical Methylcyclohexane Pyrolysis," ACS Symposium on Structure of Fuels V, ACS 216th National Meeting, Boston, MA, August 2, 1998.

Wornat, M. J., "High-Temperature Reaction Pathways Leading to Large Polycyclic Aromatic Hydrocarbons from Aromatic Fuels," ACS Symposium on Structure of Fuels V, ACS 216th National Meeting, Boston, MA, August, 2, 1998.

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SIGNIFICANT INTERACTIONS

Dr. Tim Edwards, Air Force Research Laboratory Propulsion Directorate, WPAFB, Ohio, 1999.

There were no inventions associated with the research conducted in this project.

Figure Captions

1. Supercritical Fuel Thermal Destabilization Observed to Depend on Fuel Chemistry Above 820 K
2. Chemical Structure of Endothermic Fuels
3. Major Products of Methylcyclohexane Pyrolysis at 819 K and 4.51 MPa (45.1 atm)
4. Major Products of Decalin Pyrolysis at 819 K and 4.51 MPa (45.1 atm)
5. Supercritical Flow Reactor Apparatus
- 6A,B. Possible Mechanisms of the Formation of Some of the Major Products of Decalin Decomposition including Methylhexahydroindane Formation.
- 7A,B. Suggested Mechanisms for Methylcyclohexane Pyrolysis Under Sub- And Supercritical Conditions Including the Formation of Dimethylpentanes.
8. Reaction Rate Data of Methylcyclohexane, Decalin and Tetralin Pyrolysis at 1 and 45 atm.
9. Comparison of Rates Determined from Fig. 8 and Products Under each Condition
10. Yields of Methylhexahydroindane over Methylene cyclohexene (PPM/PPM) versus Pressure. It is proposed that these products come from the same radical intermediates (pathways II and III of Fig. 6).
11. Polycyclic Aromatic Hydrocarbon Formation at 820 K, 82 atm.: HPLC Analysis Identifies Species Larger than 3-Rings.

Supercritical Fuel Thermal Destabilization Observed to Depend on Fuel Chemistry above 820 K

<i>Fuel</i>	<i>Critical Temp. (K)</i>	<i>Critical Press. (MPa.)</i>	<i>PAH Formation</i>	<i>Solid Formation</i>
Methylcyclohexane	572.2	3.471	Yes	Yes
Toluene	540.3	2.756	No	No
Heptane	591.8	4.104	Trace	Trace
10% Heptane with 90% Toluene (molar)	577.5	3.61	Yes	Yes

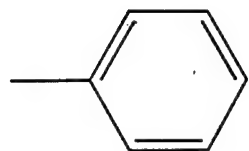
Toluene does not pyrolyze by itself below 840 K due to its high bond strengths. Pure heptane breaks down almost completely to benign gaseous products. The mix, however, is susceptible to solid formation.

FIGURE 1

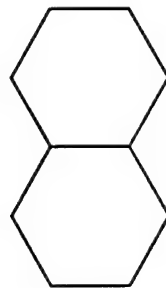
CHEMICAL STRUCTURE OF ENDOTHERMIC FUELS



Methylcyclohexane

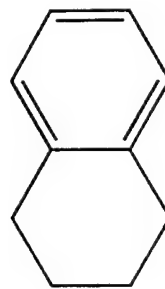


Toluene



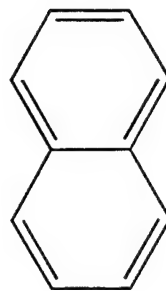
Decalin

decahydronaphthalene



Tetralin

tetrahydronaphthalene



Naphthalene

FIGURE 2

Major Products of Methylcyclohexane Pyrolysis

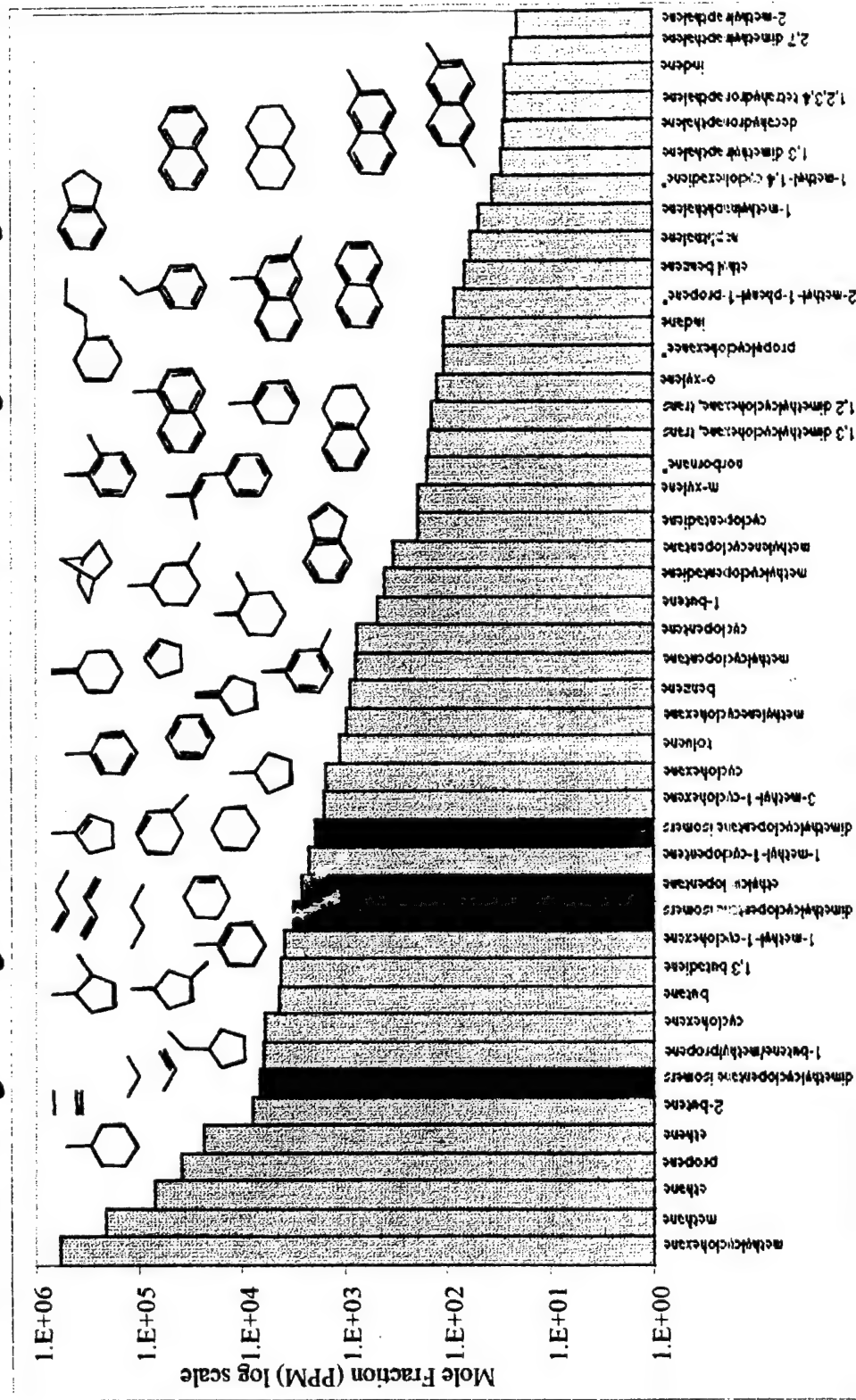


FIGURE 3

Major Products of Supercritical Decalin Pyrolysis

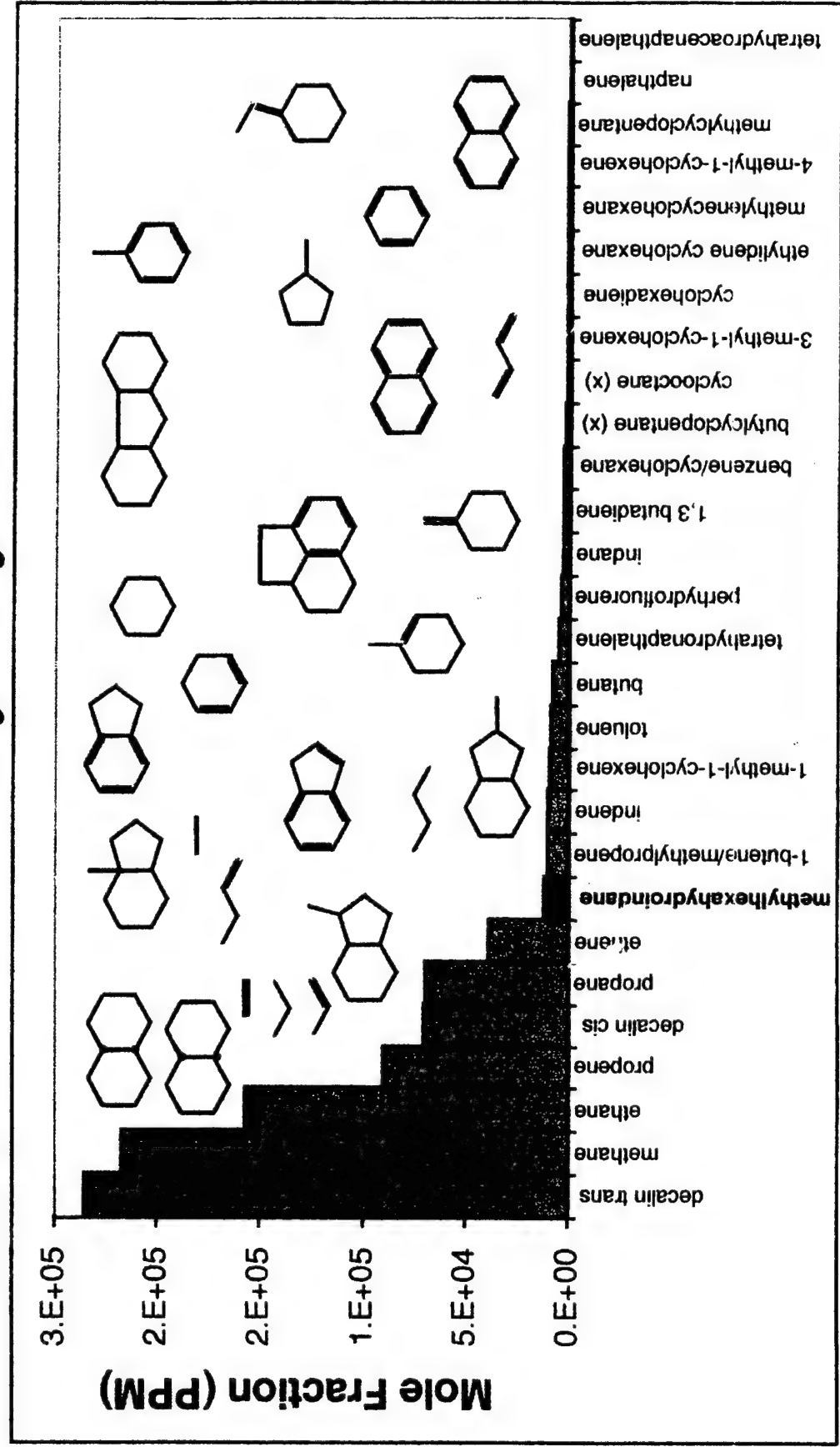


FIGURE 4

Experimental Apparatus

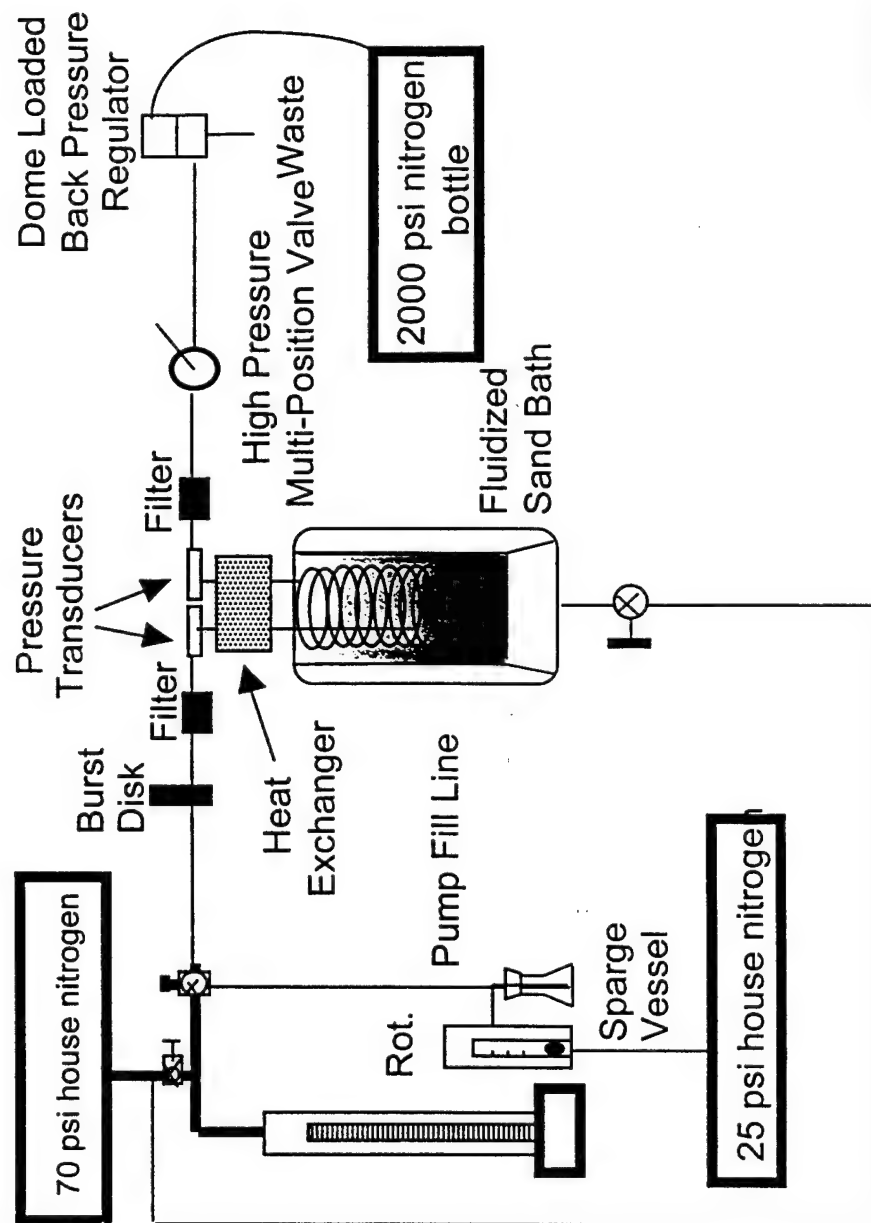


FIGURE 5

Decalin Pyrolysis Gas Phase

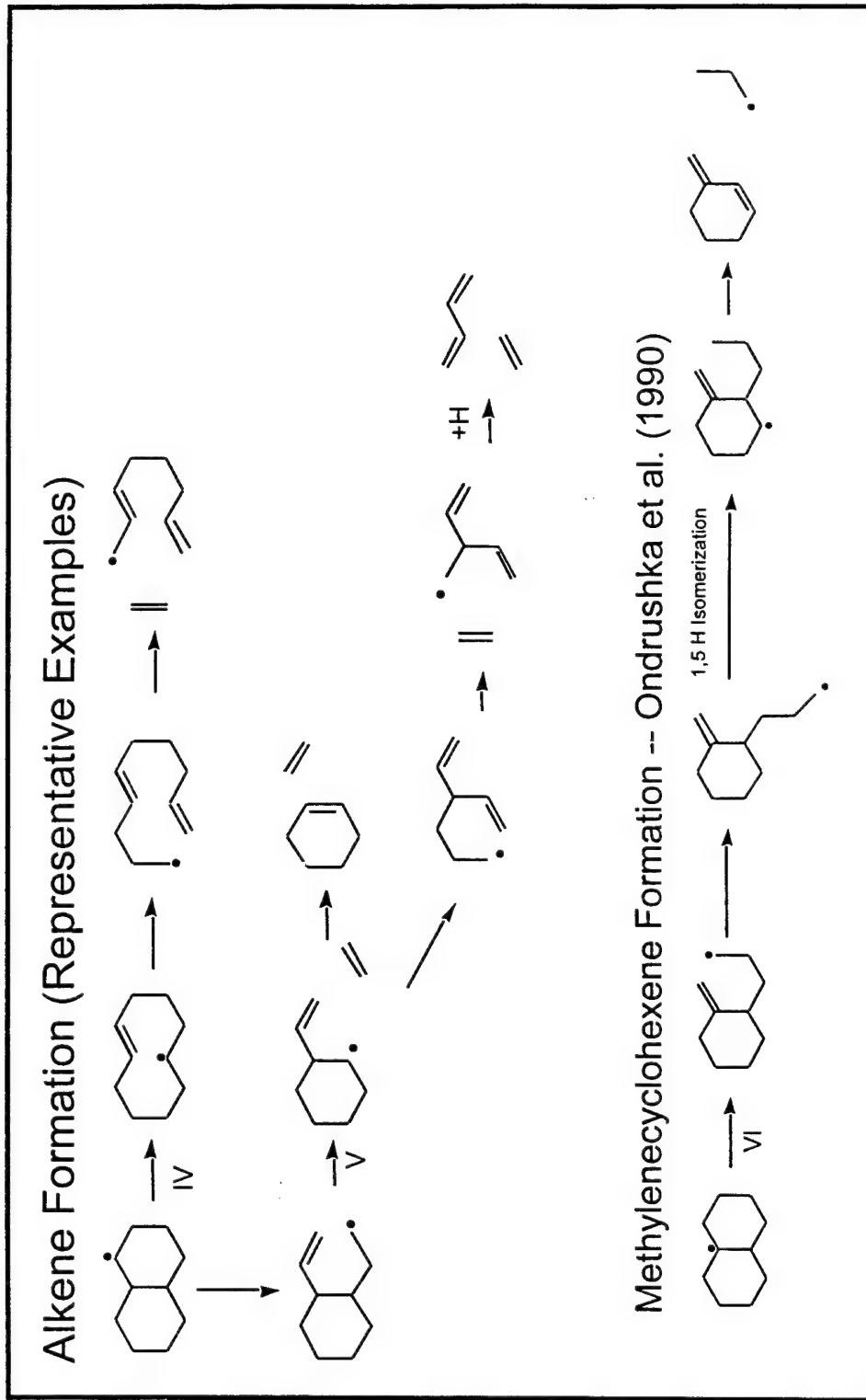


FIGURE 6A

Supercritical Decalin Pyrolysis

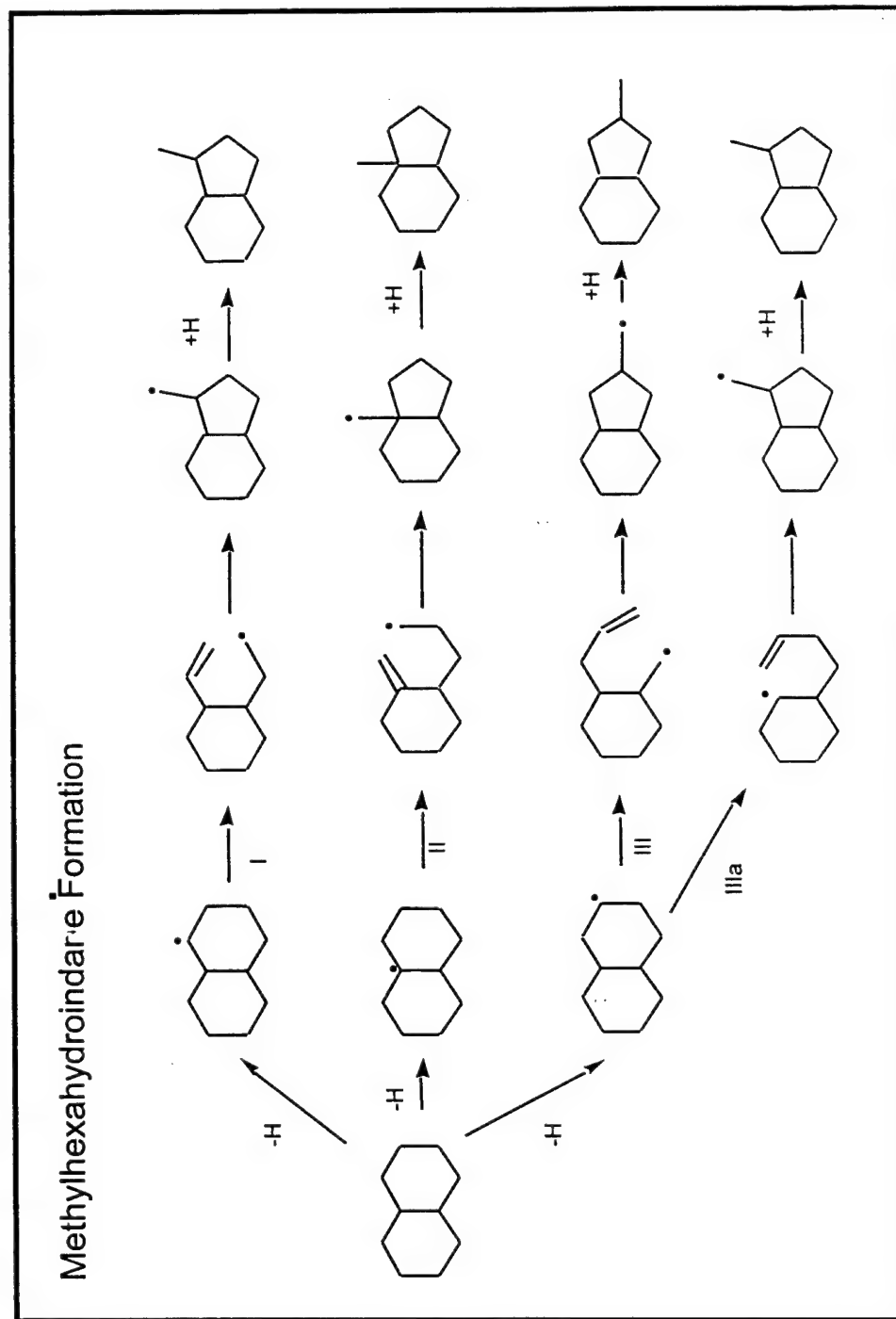


FIGURE 6B

MCH PYROLYSIS MECHANISMS

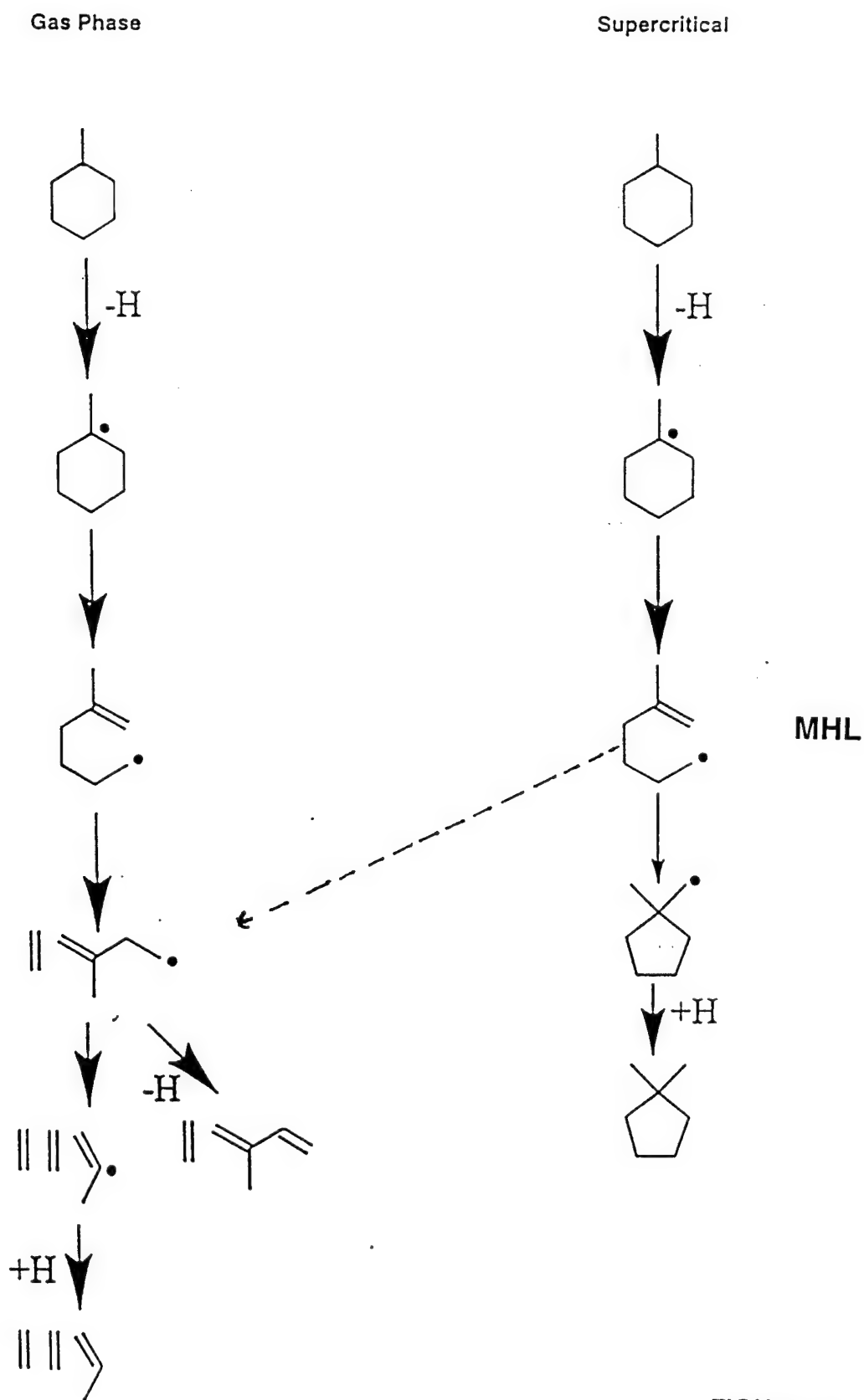


FIGURE 7.

Global Kinetic Rates

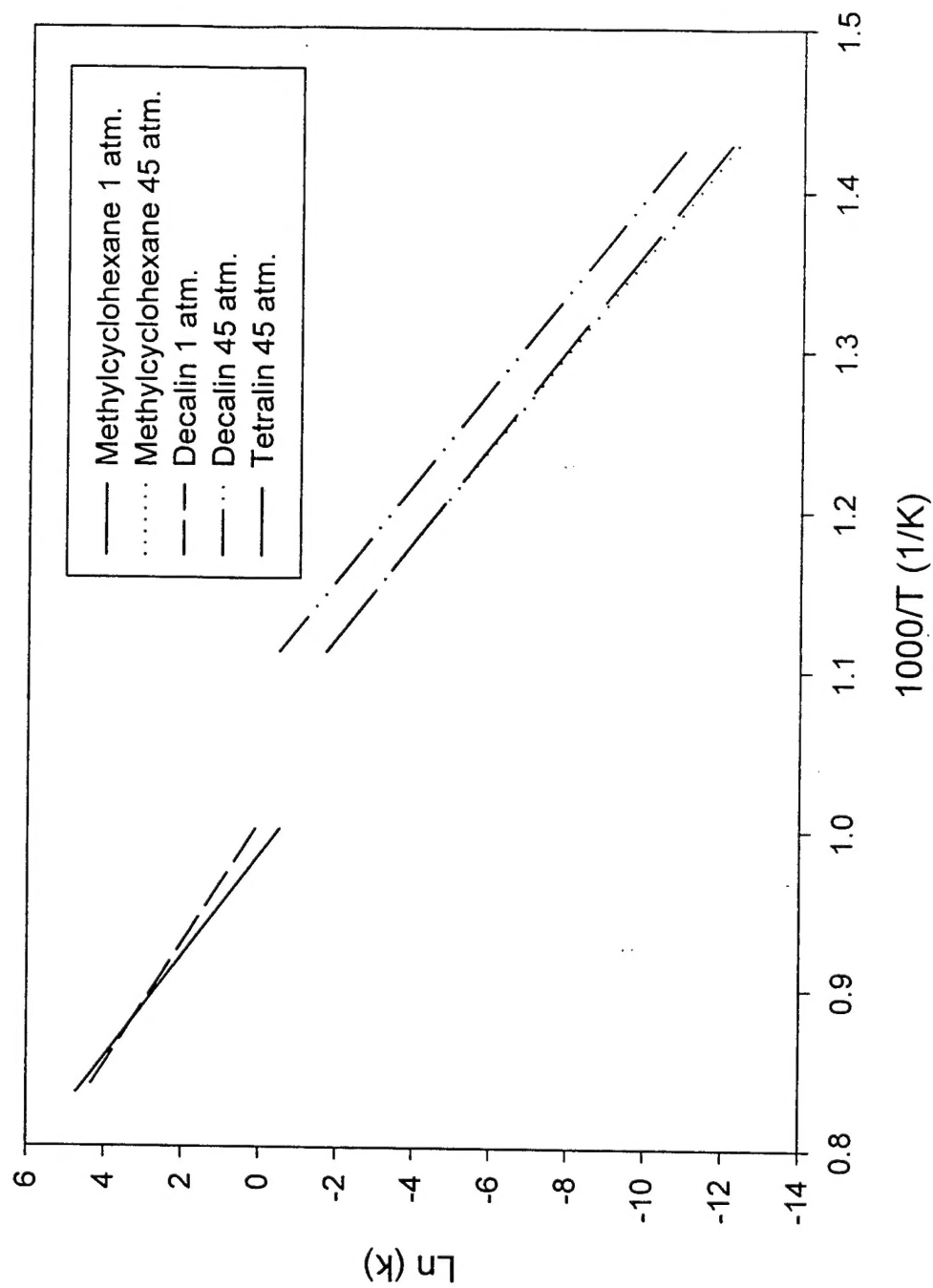


FIGURE 8

Integrated Research Summary

<i>Fuel</i>	<i>Phase</i>	<i>A (1/sec)</i>	<i>Ea (kJ/mole)</i>	<i>Major Products</i>
Methylcyclohexane	gas	2.55E+13	261	ethene, 1,3 butadiene, methane, propene
Methylcyclohexane	supercritical	2.51E+15	278	methane, ethane, propene, ethene, dimethylcyclopentane , propane, 1-methyl-1-cyclohexene, ethylcyclopentane
Decalin	gas	2.70E+11	218	methane, ethene, propene, 1,3 butadiene, benzene, toluene
Decalin	supercritical	6.31E+15	276	methane, propane, ethane, propene, ethene, butene, butane, methylhexahydroindane , indene
Tetralin	supercritical	1.26E+15	273	naphthalene, methylindane , ethane, methane, ethene, phenylbutane, propane, propene

FIGURE 9

Effects of Supercriticality (Caging)

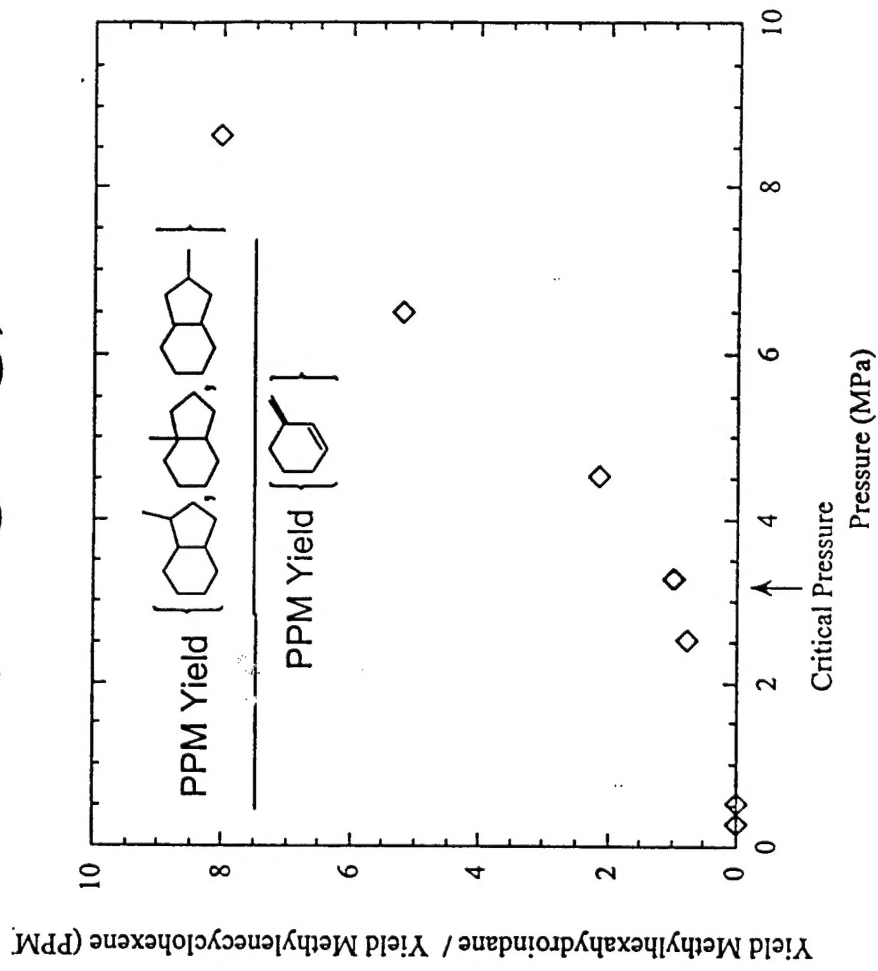


FIGURE 10

Polycyclic Aromatic Hydrocarbon Formation at 820K, 82 atm.: HPLC Analysis Identifies Species Larger Than 3-Rings

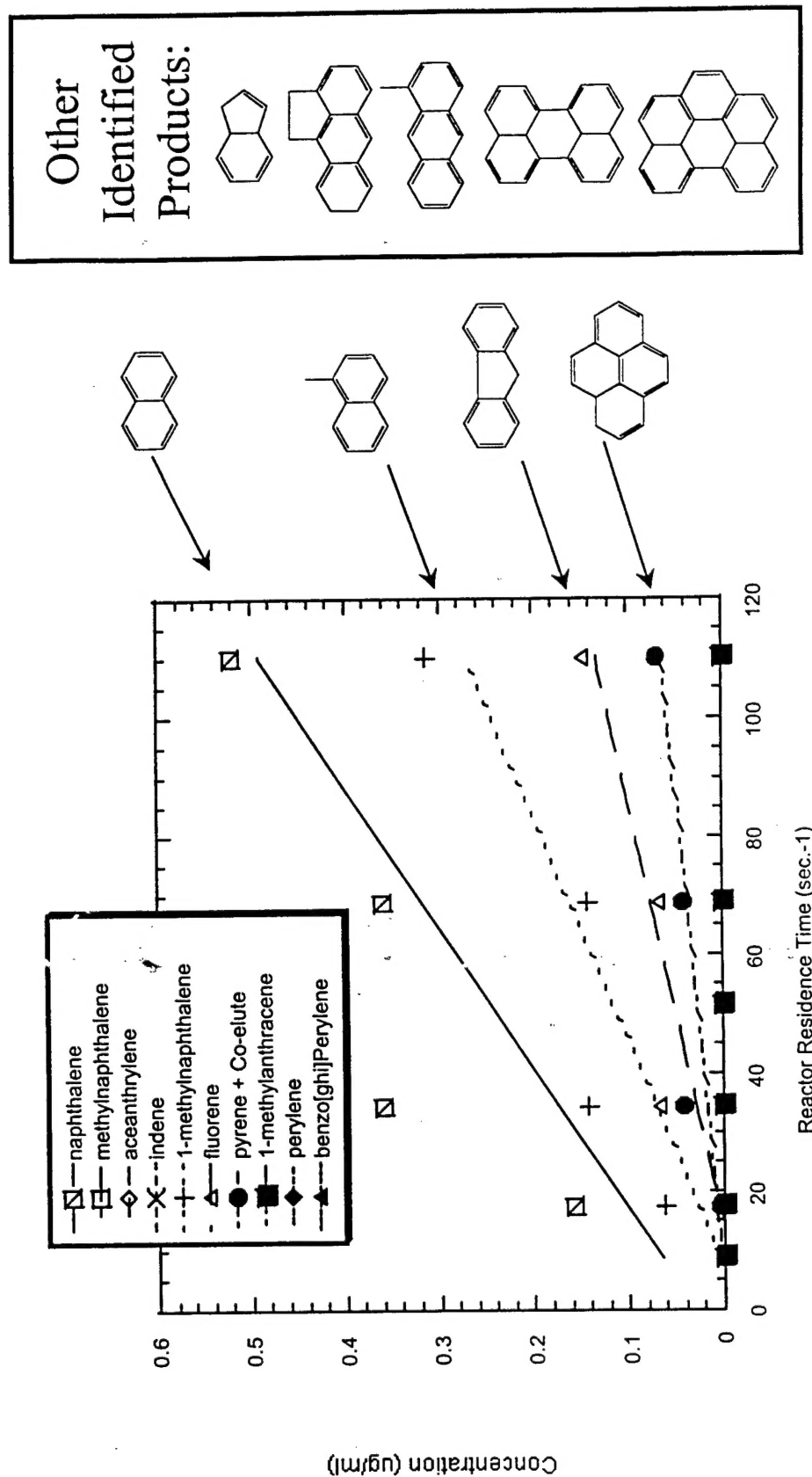


FIGURE 11